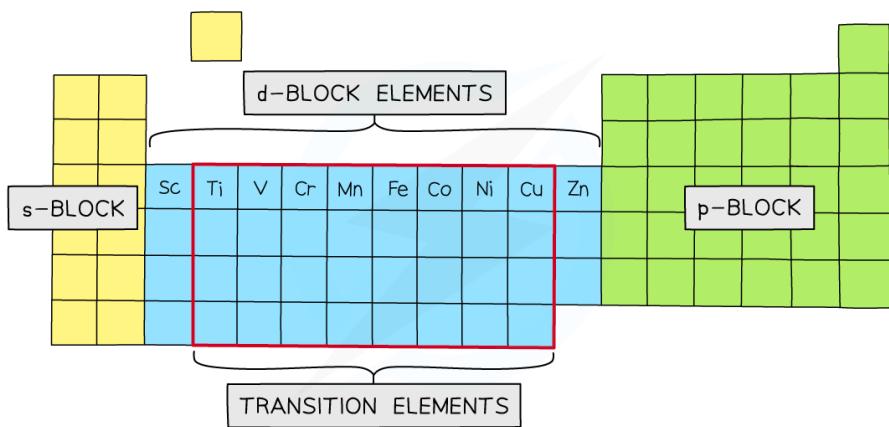


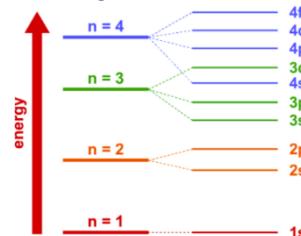
Topic 17: Transition Metals and their Chemistry

Students will be assessed on their ability to:

17.1	know that transition metals are <i>d</i> -block elements that form one or more stable ions with incompletely-filled <i>d</i> -orbitals
	<p>Transition metals are <i>d</i>-block elements that form one or more stable ions with incompletely-filled <i>d</i>-orbitals</p>  <p>Copyright © Save My Exams. All Rights Reserved</p> <p>Notice that Sc and Zn are d-block elements but are not transition metals because Sc can only form Sc^{3+} which has an empty 3d-orbital while Zn can only form Zn^{2+} which has a complete 3d-orbital</p>
17.2	be able to deduce the electronic configurations of atoms and ions of the <i>d</i> -block elements of Period 4 (Sc-Zn) given their atomic number and charge (if any)

Atomic Number	Symbol	1s	2s	2p	3s	3p	3d	4s	4p
1	H	1							
2	He	2							
3	Li	2	1						
4	Be	2	2						
5	B	2	2	1					
6	C	2	2	2					
7	N	2	2	3					
8	O	2	2	4					
9	F	2	2	5					
10	Ne	2	2	6					
11	Na	2	2	6	1				
12	Mg	2	2	6	2				
13	Al	2	2	6	2	1			
14	Si	2	2	6	2	2			
15	P	2	2	6	2	3			
16	S	2	2	6	2	4			
17	Cl	2	2	6	2	5			
18	Ar	2	2	6	2	6			
19	K	2	2	6	2	6		1	
20	Ca	2	2	6	2	6		2	
21	Sc	2	2	6	2	6	1	2	
22	Ti	2	2	6	2	6	2	2	
23	V	2	2	6	2	6	3	2	
24	Cr	2	2	6	2	6	5	1	
25	Mn	2	2	6	2	6	5	2	
26	Fe	2	2	6	2	6	6	2	
27	Co	2	2	6	2	6	7	2	
28	Ni	2	2	6	2	6	8	2	

- The Aufbau Principle states that the lowest energy sub-levels are occupied first.
- This means that the 1s sub-level is filled first, followed by 2s, 2p, 3s and 3p.
- The 4s sub-level is lower in energy than 3d, so this will fill first.



29	Cu	2	2	6	2	6	10	1	
30	Zn	2	2	6	2	6	10	2	
31	Ga	2	2	6	2	6	10	2	1
32	Ge	2	2	6	2	6	10	2	2
33	As	2	2	6	2	6	10	2	3
34	Se	2	2	6	2	6	10	2	4
35	Br	2	2	6	2	6	10	2	5
36	Kr	2	2	6	2	6	10	2	6

17.3

understand why transition metals show variable oxidation number

General properties of transition metals

Physical Properties	Chemical Properties
Variable Oxidation States	<i>Catalytic behaviour</i>
	<i>Coloured compounds</i>
	<i>Complex ions formation</i>

When transition elements form ions, they lose electrons from the 4s subshell first before their 3d electrons

- This is because when the orbitals are occupied, the repulsion between electrons pushes the 4s into a higher energy state so that it becomes slightly higher in energy than the 3d subshell

Each element can lose a variable number of electrons and so forms ions with variable oxidation numbers

- Higher oxidation numbers are not found in simple ions
- Higher oxidation numbers usually are found in transition metal ions containing an electronegative element like oxygen

17.4

know what is meant by the term 'ligand'

Ligand

is a species (molecule or ion) that forms a dative (coordinate) covalent bond with a transition metal (atom or ion) by donating a pair of electrons to the bond

- Ligands are electron-rich species (like a nucleophile) that can form dative bonds
- Ligands are mostly negatively charged and have a lone pair of electrons
- **Coordination number** is the number of dative covalent bonds to the central metal atom or ion (can be one, two or multiple)

17.5

understand that dative (coordinate) covalent bonding is involved in the formation of complex ions

Ligand	Formula	Charge	Name in complex
Water	H ₂ O	0	Aqua
Hydroxide	OH ⁻	-1	Hydroxo
Ammonia	NH ₃	0	Ammine
Chloride	Cl ⁻	-1	Chloro
Cyanide	CN ⁻	-1	Cyano

Formation of Complex Ions

A complex is a central metal ion surrounded by ligands

Dative (coordinate) bonding is involved in complex formation

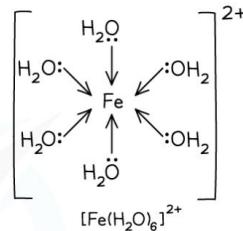
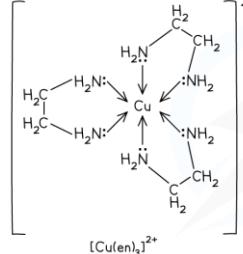
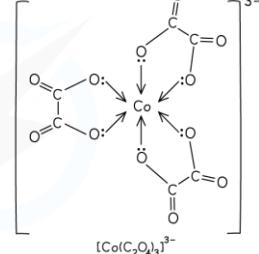
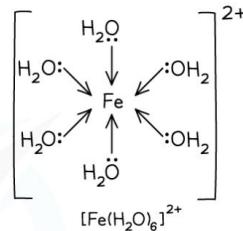
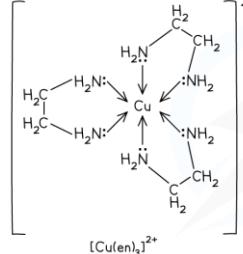
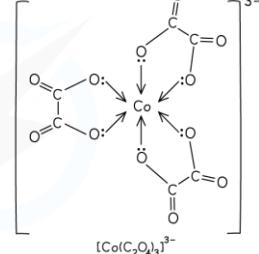
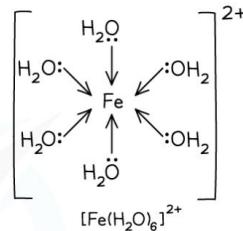
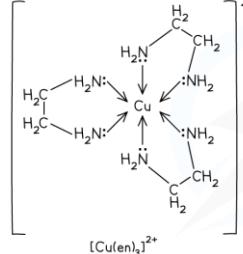
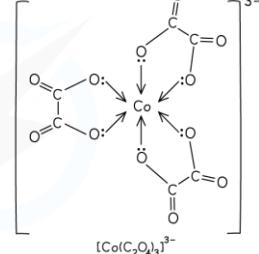
- Dative bonding is when the shared pair of electrons in the covalent bond come from only one of the bonding atoms

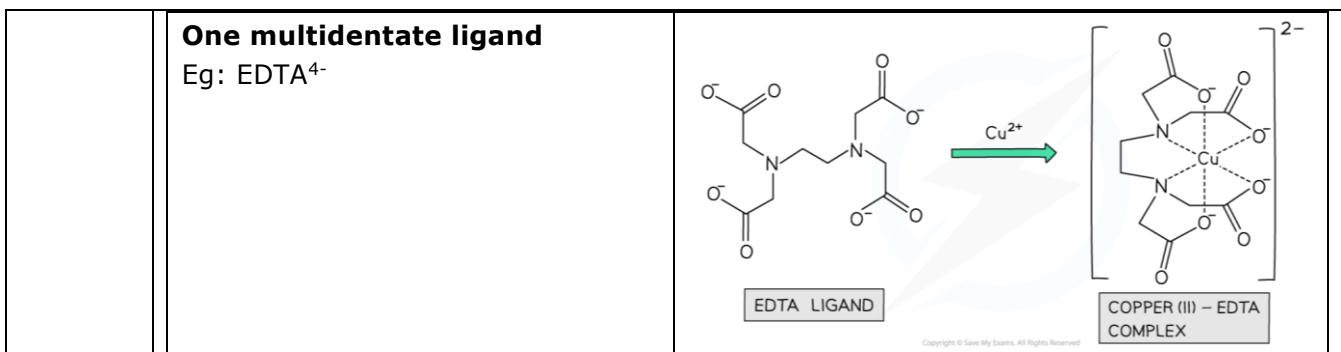
17.6

know that a complex ion is a central metal ion surrounded by ligands

	<p>A complex ion is a central metal ion surrounded by ligands (with an overall positive or negative charge)</p> <p>The geometrical arrangement of complex ions is represented by square brackets</p> <p>The overall charge on the complex ion is the sum of the oxidation states of all the species present</p> <p>If the ligands are neutral, the overall charge will be the same as the oxidation state of the metal ion</p>

17.7	know that aqueous solutions of transition metal ions are usually coloured
	<p>Colour in Aqueous Ions</p> <p>The colors of transition metal complexes arise from <i>electronic transitions between different energy levels of the d-orbitals</i>, where specific wavelengths of light are absorbed, and the complementary color is observed (due to transmitted light, light that is not absorbed)</p> <p>(by complementary, it means two colours directly opposite each other in the colour wheel)</p>
17.8	understand that the colour of aqueous ions, and other complex ions, is a consequence of the splitting of the energy levels of the d-orbitals by ligands
	<p>How Colour Arises</p> <p>In a transition metal atom, the five orbitals that make up the d-subshell all have the same energy and all transition metal ions have a partially filled 3d energy level</p> <p>1. D-orbital splitting</p> <p>In a transition metal complex, the ligands surrounding the metal ion interact with the d-orbitals, causing them to split into different energy levels</p> <p>2. Electronic transition</p> <p>When light is incident on the complex ion, electrons can be excited or promoted (jump) from lower to higher energy d-orbitals by absorbing specific wavelengths of light</p> <p>3. Colour perception</p> <p>A portion of visible light is absorbed to promote d-electrons to higher energy levels and the light that is not absorbed is transmitted to give the substance colour</p> <p>The color we perceive is the complementary color of the absorbed light</p> <p>Changing Colour</p> <p>Changing a ligand or changing the coordination number will alter the energy split between the d- orbitals, changing ΔE and hence change the wavelength of light absorbed</p>
17.9	understand why there is a lack of colour in some aqueous ions and other complex ions
	<p>Aqueous and Complex ions without colour</p> <p>Ions that have completely-filled 3d energy levels (like Zn^{2+}) and ions that have no electrons in their 3d subshells (like Sc^{3+}) are not coloured</p>

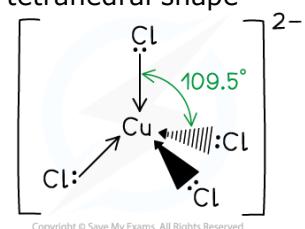
	<ul style="list-style-type: none"> - Scandium is a member of the d block, its ion (Sc^{3+}) hasn't got any d-electrons left to move around and so there is not an energy transfer equal to that of visible light - In the case of Zn^{2+} ions and Cu^+ ions the d shell is full E.g: $3d^{10}$ so here there is no space for electrons to transfer and so there is not an energy transfer equal to that of visible light 							
17.10	understand the meaning of the term 'coordination number'							
	Coordination number is the <i>number of dative covalent bonds to the central metal atom or ion</i> (can be one, two or multiple)							
17.11	understand that colour changes in transition metal ions may arise as a result of changes in: <ol style="list-style-type: none"> oxidation number of the ion ligand coordination number of the complex 							
i	Factors affecting colour changes: <ol style="list-style-type: none"> Oxidation state $[\text{Co}(\text{NH}_3)_6]^{2+}(\text{aq}) \rightarrow [\text{Co}(\text{NH}_3)_6]^{3+}(\text{aq}) + \text{e}^-$ <table style="width: 100%; text-align: center;"> <tr> <td>Yellow</td> <td>(standing in air) O_2</td> <td>Brown</td> </tr> </table> <ol style="list-style-type: none"> Ligand $[\text{Co}(\text{H}_2\text{O})_6]^{2+} + 6\text{NH}_3 \rightarrow [\text{Co}(\text{NH}_3)_6]^{2+} + 6\text{H}_2\text{O}$ <table style="width: 100%; text-align: center;"> <tr> <td>Pink</td> <td>Yellow-brown</td> </tr> </table> <ol style="list-style-type: none"> Coordination number of the complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}$ <table style="width: 100%; text-align: center;"> <tr> <td>Blue</td> <td>Green</td> </tr> </table>	Yellow	(standing in air) O_2	Brown	Pink	Yellow-brown	Blue	Green
Yellow	(standing in air) O_2	Brown						
Pink	Yellow-brown							
Blue	Green							
17.12	understand that H_2O , OH^- and NH_3 act as monodentate ligands							
	Monodentate ligands <ul style="list-style-type: none"> - Can form only one dative bond to the central metal ion because they only have one lone pair of electrons - Examples: H_2O, OH^-, CN^-, Cl^- and NH_3 							
17.13	understand why complexes with six-fold coordination have an octahedral shape, such as those formed by metal ions with H_2O , OH^- and NH_3 as ligands							
	Octahedral complexes are formed when a central metal atom or ion forms six dative covalent (coordinate) bonds <ul style="list-style-type: none"> - The bond angles in an octahedral complex are 90 - It could be six dative covalent bonds with: <table style="margin-left: 20px; border-collapse: collapse;"> <tr> <td style="vertical-align: top;"> Six small, monodentate ligands Eg: H_2O and NH_3 They have six-fold coordination </td> <td style="vertical-align: top; padding-left: 20px;">  </td> </tr> </table> <table style="margin-left: 20px; border-collapse: collapse;"> <tr> <td style="vertical-align: top;"> Three bidentate ligands Eg: 1,2-diaminoethane and ethanedioate ion </td> <td style="vertical-align: top; padding-left: 20px;">  </td> <td style="vertical-align: top; padding-left: 20px;">  </td> </tr> </table> 	Six small, monodentate ligands Eg: H_2O and NH_3 They have six-fold coordination		Three bidentate ligands Eg: 1,2-diaminoethane and ethanedioate ion				
Six small, monodentate ligands Eg: H_2O and NH_3 They have six-fold coordination								
Three bidentate ligands Eg: 1,2-diaminoethane and ethanedioate ion								



17.14 know that transition metal ions may form tetrahedral complexes with relatively large ions such as Cl^-

Tetrahedral Complexes are formed when a central metal atom or ion forms four dative covalent (coordinate) bonds and they often have a tetrahedral shape

- **Complexes with four Cl^- ions** most commonly adopt this shape
- Chloride ligands are large, so only four will fit around the central metal ion
- The bond angles in a tetrahedral complex are 109.5

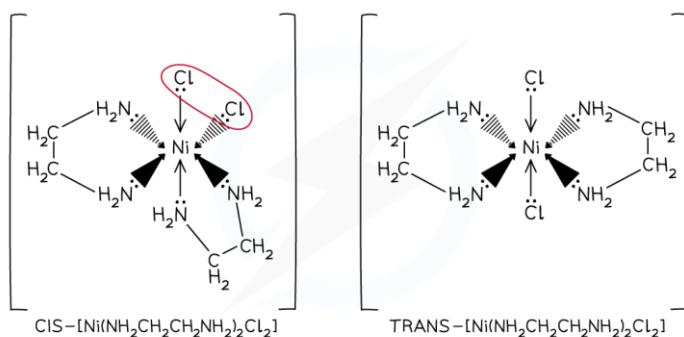


17.15 know that square planar complexes are also formed by transition metal ions and that *cis*-platin is an example of such a complex which is used in cancer treatment where it is supplied as a single isomer and not in a mixture with the *trans* form

Stereoisomerism

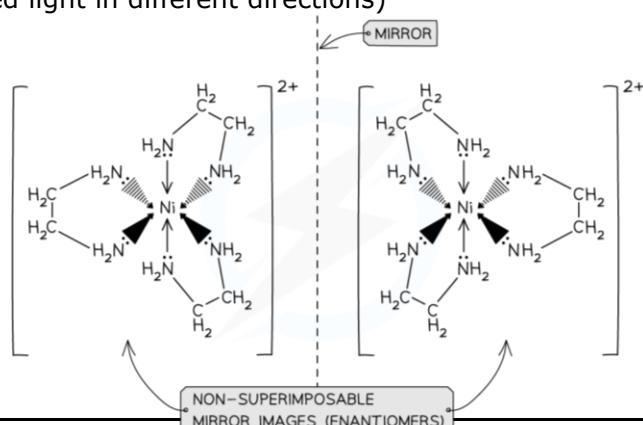
Geometric Isomerism

Square planar and **octahedral complexes** with two pairs of different ligands exhibit cis-trans isomerism even though they do not have a double bond



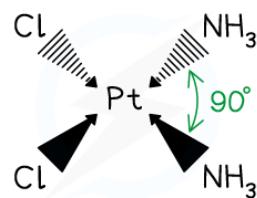
Optical Isomerism

Octahedral complexes with bidentate ligands exhibit optical isomerism (which means they can form non-superimposable mirror images of each other and they rotate plane polarised light in different directions)



Square planar complexes

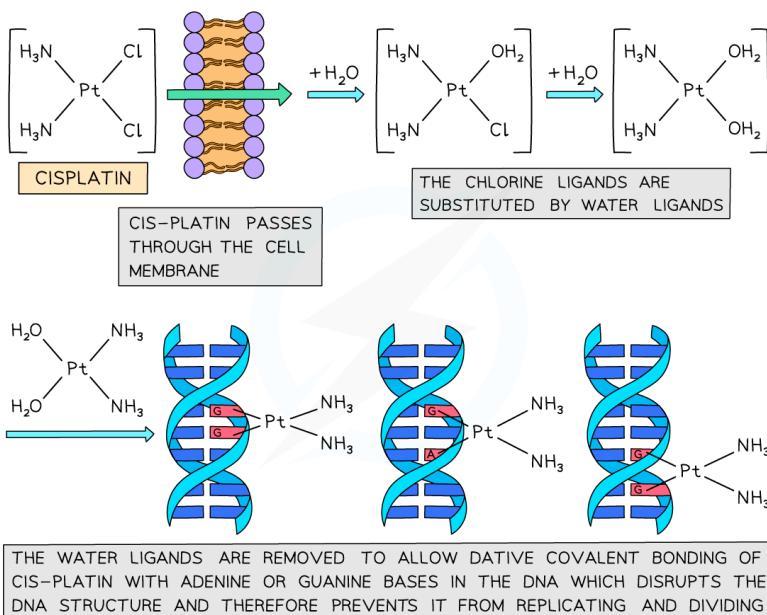
- Complexes with **four coordinate bonds** may adopt a **square planar** geometry instead of a tetrahedral one
 - Cyanide ions (CN^-) are the most common ligands to adopt this geometry
 - An example of a square planar complex is **cisplatin**
- The bond angles in a square planar complex are 90°



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Cisplatin

- The Pt(II) complex **cis-platin** is used in cancer treatment
- trans-platin cannot be used in cancer treatment**
- Only cisplatin works as two chlorine atoms are displaced by water molecules (ligand exchange) and the molecule joins on to the DNA of cancer cells and in doing so, it stops the replication of cancer cells



17.16	understand the terms 'bidentate' and 'hexadentate' in relation to ligands, and be able to identify examples such as $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and EDTA^{4-}
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Bidentate Ligands

- Can form two dative bonds to the central metal ion because each ligand contains two atoms with lone pairs of electrons
- Examples: $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (a.k.a) "en" and $\text{C}_2\text{O}_4^{2-}$ (a.k.a) "ox"

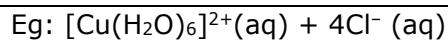
Multidentate Ligands

- Can form more than two dative bonds to the central metal ion because some ligands contain more than two atoms with lone pairs of electrons
- Examples: Hexadentate – EDTA^{4-} (forms 6 dative bonds to central ion)

17.17	know that haemoglobin is an iron(II) complex containing a polydentate ligand and that ligand exchange occurs when an oxygen molecule bound to haemoglobin is replaced by a carbon monoxide molecule
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Exchanging Ligands

- Ligand exchange is when one ligand in a complex is replaced (substituted) by another ligand and forms a new complex that is more stable than the original
- Ligands can be partially or entirely substituted
- The charge of the complex ion can change or not depending on the ligand
- If the ligands are of similar size, there are no changes in coordination number or the geometry of the complex
- If they are different sizes (like Cl^- and H_2O), then there are changes



Haemoglobin & Ligand Exchange

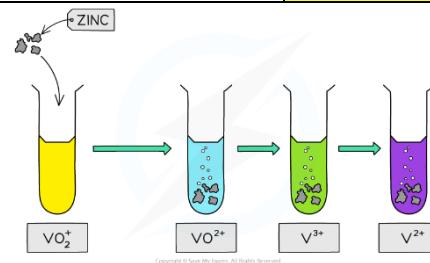
- 17.18** know the colours of the oxidation states of vanadium (+5, +4, +3 and +2) in its compounds

Vanadium - Colours & Oxidation States

Oxidation No.	Formula	Name	Colour of aq. sol
+2	V^{2+}	Vanadium (II)	Purple
+3	V^{3+}	Vanadium (III)	Green
+4	VO^{2+}	Oxovanadium (IV)	Blue
+5	VO_2^{+}	Dioxovanadium (V)	Yellow

We can see this change by the reaction of zinc with ammonium vanadate(V) under acidic conditions

Zn is a reducing agent so will reduce vanadium(V) to vanadium(II)



17.19

understand redox reactions for the interconversion of the oxidation states of vanadium (+5, +4, +3 and +2), in terms of the relevant E^\ominus values

Vanadium – Interconversion of oxidation states

Explanation using E^\ominus values

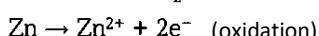
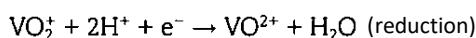
	Redox equation	E^\ominus value
1.	$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$	-1.18 V
2.	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76 V
3.	$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	-0.26 V
4.	$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34 V
5.	$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00 V

Strongest reducing agent (most negative E value)

Strongest oxidizing agent (most positive E value)

We can obtain the overall equation by combining the half equations and ensuring the same no. of electrons in both equations

Reduction from +5 to +4 by Zn

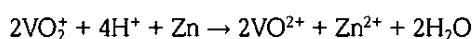


(Half-equation 5 and 2)

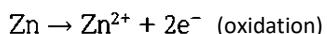
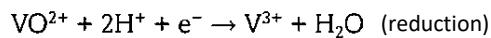
Zn is electron-releasing with respect to VO_2^+

$$E_{cell} = 1.00 + 0.76 = +1.76V$$

Overall reaction:



Reduction from +4 to +3 by Zn

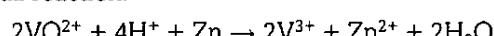


(Half-equation 4 and 2)

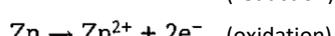
Zn is electron-releasing with respect to VO^{2+}

$$E_{cell} = 0.34 + 0.76 = +1.10V$$

Overall reaction:



Reduction from +3 to +2 by Zn

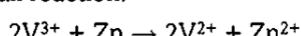


(Half-equation 3 and 2)

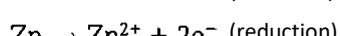
Zn is electron-releasing with respect to V^{3+}

$$E_{cell} = -0.26 + 0.76 = +0.50V$$

Overall reaction:



Reduction from +2 to 0 by Zn

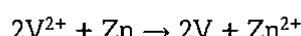


(Half-equation 1 and 2)

Zn is not electron-releasing with respect to V^{2+}

Thus, reaction is not thermodynamically feasible

$$E_{cell} = -1.18 - 0.76 = -1.94V$$



17.20	understand, in terms of the relevant E values, that the dichromate(VI) ion, $\text{Cr}_2\text{O}_7^{2-}$ i can be reduced to Cr^{3+} and Cr^{2+} ions using zinc in acidic conditions ii can be produced by the oxidation of Cr^{3+} ions using hydrogen peroxide in alkaline conditions (followed by acidification)
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i	<p>Chromium – Reduction & Oxidation</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="background-color: #c8f7e4;"></th><th style="background-color: #c8f7e4;">Redox equation</th><th style="background-color: #c8f7e4;">E^\ominus value</th></tr> </thead> <tbody> <tr> <td style="text-align: center;">1.</td><td>$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$</td><td style="text-align: center;">−0.76 V</td></tr> <tr> <td style="text-align: center;">2.</td><td>$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cr}^{2+}(\text{aq})$</td><td style="text-align: center;">−0.41 V</td></tr> <tr> <td style="text-align: center;">3.</td><td>$\text{CrO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) + 3\text{e}^- \rightleftharpoons \text{Cr(OH)}_3(\text{aq}) + 5\text{OH}^-(\text{aq})$</td><td style="text-align: center;">−0.13 V</td></tr> <tr> <td style="text-align: center;">4.</td><td>$\text{H}_2\text{O}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{OH}^-(\text{aq})$</td><td style="text-align: center;">+1.24 V</td></tr> <tr> <td style="text-align: center;">5.</td><td>$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$</td><td style="text-align: center;">+1.33 V</td></tr> </tbody> </table> <p style="text-align: center; font-size: small;">Copyright © Tessa Mo Farrooqi. All Rights Reserved.</p> <p>Reduction from +6 to +3 by Zn</p> $3\text{Zn} \rightleftharpoons 3\text{Zn}^{2+} + 6\text{e}^- \quad (\text{oxidation}) \quad (\text{Half-equation 1 and 5})$ $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad (\text{reduction})$ <p>Zn is electron-releasing with respect to $\text{Cr}_2\text{O}_7^{2-}$</p> $E_{\text{cell}} = 1.33 + 0.76 = +2.09\text{V}$ <p>Overall equation is:</p> $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 3\text{Zn} \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{Zn}^{2+}$ <p>!This reaction is carried out under acidic conditions due to the presence of H^+ in the equation</p> <p>Reduction from +3 to +2 by Zn</p> $\text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2\text{e}^- \quad (\text{oxidation}) \quad (\text{Half-equation 1 and 2})$ $2\text{Cr}^{3+} + 2\text{e}^- \rightleftharpoons 2\text{Cr}^{2+} \quad (\text{reduction})$ <p>Zn is electron-releasing with respect to $\text{Cr}_2\text{O}_7^{2-}$</p> $E_{\text{cell}} = 1.33 + 0.76 = +2.09\text{V}$ <p>Overall reaction is: $2\text{Cr}^{3+} + \text{Zn} \rightleftharpoons 2\text{Cr}^{2+} + \text{Zn}^{2+}$</p>		Redox equation	E^\ominus value	1.	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	−0.76 V	2.	$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cr}^{2+}(\text{aq})$	−0.41 V	3.	$\text{CrO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) + 3\text{e}^- \rightleftharpoons \text{Cr(OH)}_3(\text{aq}) + 5\text{OH}^-(\text{aq})$	−0.13 V	4.	$\text{H}_2\text{O}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{OH}^-(\text{aq})$	+1.24 V	5.	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.33 V
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ii	<p>Oxidation from +3 to +6 by H_2O</p> $2\text{Cr(OH)}_3 + 10\text{OH}^- \rightleftharpoons 2\text{CrO}_4^{2-} + 8\text{H}_2\text{O} + 6\text{e}^- \quad (\text{oxidation}) \quad (\text{Half-equation 3 and 4})$ $3\text{H}_2\text{O}_2 + 6\text{e}^- \rightleftharpoons 6\text{OH}^- \quad (\text{reduction})$ $E_{\text{cell}} = −0.41 + 1.24 = 0.83\text{V}$ <p>Overall reaction is:</p> $2\text{Cr(OH)}_3 + 4\text{OH}^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{CrO}_4^{2-} + 8\text{H}_2\text{O}$ <p>!This reaction is carried out under alkaline conditions due to the presence of OH^- in the equation</p>
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Colour Changes of Chromium Summary	
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17.21	know that the dichromate(VI) ion, $\text{Cr}_2\text{O}_7^{2-}$ can be converted into chromate(VI) ions as a result of the equilibrium: $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{CrO}_4^{2-} + 2\text{H}^+$		
	<p>Conversion between dichromate(VI) ion $\text{Cr}_2\text{O}_7^{2-}$ and chromate(VI) ion CrO_4^{2-}</p> $2\text{CrO}_4^{2-} (\text{aq}) + 2\text{H}^+ (\text{aq}) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} (\text{aq}) + \text{H}_2\text{O} (\text{l})$ <table style="width: 100%; text-align: center;"> <tr> <td style="width: 50%;">Yellow solution</td> <td style="width: 50%;">Orange solution</td> </tr> </table> <ul style="list-style-type: none"> - <i>Chromate(VI) ions are stable in alkaline solution but in acidic conditions, dichromate(VI) ions are more stable</i> - Addition of acid will push equilibrium to the dichromate - Addition of alkali will remove the H^+ ions and push equilibrium to the chromate - This is an acid-base reaction (not redox) 	Yellow solution	Orange solution
Yellow solution	Orange solution		

17.22	be able to record observations and write suitable equations for the reactions of Cr^{3+} (aq), Mn^{2+} (aq), Fe^{2+} (aq), Fe^{3+} (aq), Co^{2+} (aq), Ni^{2+} (aq), Cu^{2+} (aq) and Zn^{2+} (aq) with aqueous sodium hydroxide and aqueous ammonia, including in excess																																				
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17.23	<p>be able to write ionic equations to show the meaning of amphoteric behaviour, deprotonation and ligand exchange in the reactions in 17.22</p>
	<p>Reaction with limited OH⁻ and NH₃</p> <ul style="list-style-type: none"> - Deprotonation acid base reactions (not ligand substitution) - The bases OH⁻ and NH₃ when in limited amounts form the same hydroxide precipitates - Two OH⁻ ions removing H⁺ ions from two of the water ligands converting them into water molecules $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$ $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightarrow \text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3(\text{s}) + 3\text{H}_2\text{O}(\text{l})$ - Two NH₃ removing H⁺ ions from two of the water ligands converting them into ammonium ions $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightarrow \text{Zn}(\text{OH})_2(\text{H}_2\text{O})_4(\text{s}) + 2\text{NH}_4^+(\text{aq})$ - Both ligands are acting as Bronsted-Lowry bases, accepting a proton
<p>A metal hydroxide that can act as both an acid and a base is called an amphoteric hydroxide</p>	<p>Reaction with excess OH⁻</p> <ul style="list-style-type: none"> - When an excess of NaOH is added, further deprotonation occurs only with chromium and zinc hydroxides and both dissolve $[\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3](\text{s}) + 3\text{OH}^-(\text{aq}) \rightarrow [\text{Cr}(\text{OH})_6]^{3-}(\text{aq}) \text{ green} + 3\text{H}_2\text{O}(\text{l})$ $[\text{Zn}(\text{H}_2\text{O})_4(\text{OH})_2](\text{s}) + 2\text{OH}^-(\text{aq}) \rightarrow [\text{Zn}(\text{OH})_4]^{2-}(\text{aq}) \text{ colorless} + 4\text{H}_2\text{O}(\text{l})$ - These hydroxides are classed as amphoteric hydroxides as they react with alkali to give a solution and react with acid to form the aqueous salt $[\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3](\text{s}) + 3\text{H}^+(\text{aq}) \rightarrow [\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ $[\text{Zn}(\text{H}_2\text{O})_4(\text{OH})_2](\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow [\text{Zn}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$
	<p>Reaction with excess NH₃</p> <ul style="list-style-type: none"> - Ligand exchange (substitution) reactions occur with Cu, Co and Cr and their precipitates dissolve - The ligands NH₃ and H₂O are similar in size and are uncharged so ligand exchange occurs without change of coordination number for Co and Cr Cr becomes purple solution $[\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3](\text{s}) + 6\text{NH}_3(\text{aq}) \rightarrow [\text{Cr}(\text{NH}_3)_6]^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) + 3\text{OH}^-(\text{aq})$ Co becomes pale yellow solution $[\text{Co}(\text{H}_2\text{O})_4(\text{OH})_2](\text{s}) + 6\text{NH}_3(\text{aq}) \rightarrow [\text{Co}(\text{NH}_3)_6]^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) + 2\text{OH}^-(\text{aq})$ Ni becomes blue solution $[\text{Ni}(\text{H}_2\text{O})_4(\text{OH})_2](\text{s}) + 6\text{NH}_3(\text{aq}) \rightarrow [\text{Ni}(\text{NH}_3)_6]^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) + 2\text{OH}^-(\text{aq})$ Cu becomes deep blue solution $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2](\text{s}) + 4\text{NH}_3(\text{aq}) \rightarrow [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{OH}^-(\text{aq})$

	<p>2+ Ion Summary</p> <table border="1"> <thead> <tr> <th>[M(H₂O)₆]²⁺</th> <th>[Cu(H₂O)₆]²⁺ [Co(H₂O)₆]²⁺ [Fe(H₂O)₆]²⁺ [Ni(H₂O)₆]²⁺ [Mn(H₂O)₆]²⁺ [Zn(H₂O)₆]²⁺</th> <th>green sol blue sol pink sol green sol very pale pink sol colourless sol</th> <th>M(OH)₂(H₂O)₄</th> <th>[Cu(NH₃)₄(H₂O)₂]²⁺ [Co(NH₃)₆]²⁺ [Ni(NH₃)₆]²⁺ [Zn(NH₃)₄]²⁺ [Co(NH₃)₆]³⁺ brown sol</th> </tr> </thead> <tbody> <tr> <td></td> <td></td> <td></td> <td></td> <td>Air or H₂O₂</td> </tr> <tr> <td></td> <td></td> <td></td> <td></td> <td>Fe(OH)₃(H₂O)₃ brown ppt Co(OH)₃(H₂O)₃ brown ppt Mn(OH)₃(H₂O)₃ dark brown ppt</td> </tr> </tbody> </table>	[M(H ₂ O) ₆] ²⁺	[Cu(H ₂ O) ₆] ²⁺ [Co(H ₂ O) ₆] ²⁺ [Fe(H ₂ O) ₆] ²⁺ [Ni(H ₂ O) ₆] ²⁺ [Mn(H ₂ O) ₆] ²⁺ [Zn(H ₂ O) ₆] ²⁺	green sol blue sol pink sol green sol very pale pink sol colourless sol	M(OH) ₂ (H ₂ O) ₄	[Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺ [Co(NH ₃) ₆] ²⁺ [Ni(NH ₃) ₆] ²⁺ [Zn(NH ₃) ₄] ²⁺ [Co(NH ₃) ₆] ³⁺ brown sol					Air or H ₂ O ₂					Fe(OH) ₃ (H ₂ O) ₃ brown ppt Co(OH) ₃ (H ₂ O) ₃ brown ppt Mn(OH) ₃ (H ₂ O) ₃ dark brown ppt
[M(H ₂ O) ₆] ²⁺	[Cu(H ₂ O) ₆] ²⁺ [Co(H ₂ O) ₆] ²⁺ [Fe(H ₂ O) ₆] ²⁺ [Ni(H ₂ O) ₆] ²⁺ [Mn(H ₂ O) ₆] ²⁺ [Zn(H ₂ O) ₆] ²⁺	green sol blue sol pink sol green sol very pale pink sol colourless sol	M(OH) ₂ (H ₂ O) ₄	[Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺ [Co(NH ₃) ₆] ²⁺ [Ni(NH ₃) ₆] ²⁺ [Zn(NH ₃) ₄] ²⁺ [Co(NH ₃) ₆] ³⁺ brown sol												
				Air or H ₂ O ₂												
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[Cr(H ₂ O) ₆] ³⁺	[Cr(H ₂ O) ₆] ³⁺ [Fe(H ₂ O) ₆] ³⁺	green sol yellow sol	M(OH) ₃ (H ₂ O) ₃	[Cr(NH ₃) ₆] ³⁺ Cr ₂ O ₇ ²⁻ orange sol CrO ₄ ²⁻ yellow sol												
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				Fe(OH) ₃ (H ₂ O) ₃ green ppt Cr(OH) ₃ (H ₂ O) ₃ brown ppt												
17.24	<p>understand that ligand exchange, and an accompanying colour change, occurs in the formation of:</p> <ol style="list-style-type: none"> [Cu(NH₃)₄(H₂O)₂]²⁺ from [Cu(H₂O)₆]²⁺ via Cu(OH)₂(H₂O)₄ [CuCl₄]²⁻ from [Cu(H₂O)₆]²⁺ [CoCl₄]²⁻ from [Co(H₂O)₆]²⁺ 															
	<p>Ligand Exchange to form [Cu(NH₃)₄(H₂O)₂]²⁺</p> $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2](\text{s}) + 4\text{NH}_3(\text{aq}) \rightarrow [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{OH}^-(\text{aq})$ <p>Blue precipitate dissolves to form dark blue solution</p>															
	<p>Ligand Exchange to form [CuCl₄]²⁻</p> <ul style="list-style-type: none"> Addition of concentrated HCl (or saturated NaCl) to Cu and Co aqueous ions lead to a change in coordination number from 6 to 4 $[\text{Cu}(\text{H}_2\text{O})_6] + 4\text{Cl}^-(\text{aq}) \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O}$ <p>(Initial blue changes to green, which then changes to yellow solution)</p>															

	<p>Ligand Exchange to form $[\text{CoCl}_4]^{2-}$</p> $[\text{Co}(\text{H}_2\text{O})_6] + 4\text{Cl}^-(\text{aq}) \rightarrow [\text{CoCl}_4]^{2-} + 6\text{H}_2\text{O}$ (blue solution)
17.25	<p>understand, in terms of the positive increase in ΔS_{system}, that the substitution of a monodentate ligand by a bidentate or hexadentate ligand leads to a more stable complex ion</p>
	<p>The substitution of a monodentate ligand by a bidentate (ethane-1,2-diamine) or hexadentate ligand (EDTA^{4-}) leads to a more stable complex ion because:</p> <ul style="list-style-type: none"> - There are more moles of products than reactants - This leads to an increase in ΔS_{system} (more positive)
17.26	<p>know that transition metals and their compounds can act as heterogeneous and homogeneous catalysts</p>
	<p>Transition metals and their compounds can act as heterogeneous and homogeneous catalysts</p>
17.27	<p>know that a heterogeneous catalyst is in a different phase from the reactants and that the reaction occurs at the surface of the catalyst</p> <p>A heterogeneous catalyst</p> <ul style="list-style-type: none"> - is in a different phase (physical state) from the reactants - is usually a solid whereas the reactants are gaseous or in solution - reaction occurs at the surface (active site) of the catalyst <ol style="list-style-type: none"> 1. <i>Adsorption</i>: one or more reactants is attached to the surface of the catalyst 2. <i>Reaction</i>: weakening of the bonds in the adsorbed reactants 3. <i>Desorption</i>: product becomes detached from the surface of the catalyst - Strength of absorption: Ni and Pt have about the right strength and are most useful as catalysts - Increasing the surface area of a solid catalyst will improve its effectiveness <p>Advantages of heterogeneous catalysts</p> <ul style="list-style-type: none"> • Heterogeneous catalysts can be filtered off and are easy to separate from any liquid or gaseous products • They are also suited to continuous processes rather than batch processes <p>Impurities</p> <ul style="list-style-type: none"> • The effectiveness of a heterogenous catalyst can be decreased by the presence of impurities in the gas involved in the reaction
17.28	<p>understand, in terms of oxidation number, how V_2O_5 acts as a catalyst in the contact process</p> <p>Catalysis of the Contact Process (Manufacture of sulfuric acid)</p> <p>Step 1: Making SO_2: Sulfur is burned in air to produce sulfur dioxide</p> $\text{S (s)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$ <p>Step 2: Converting SO_2 to SO_3: Sulfur dioxide and oxygen are passed over the vanadium(V) oxide catalyst at an optimal temperature and pressure</p> $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ <ul style="list-style-type: none"> - The vanadium(V) oxide catalyst converts SO_2 into SO_3 and is reduced to vanadium(IV) oxide - The oxidation number of the vanadium decreases from +5 to +4 - $\text{SO}_2(\text{g}) + \text{V}_2\text{O}_5(\text{s}) \rightarrow \text{V}_2\text{O}_4(\text{s}) + \text{SO}_3(\text{g})$ - The vanadium(V) oxide is then re-generated by reaction with oxygen, fulfilling its role as a catalyst: $\text{O}_2(\text{g}) + 2\text{V}_2\text{O}_4(\text{s}) \rightarrow 2\text{V}_2\text{O}_5(\text{s})$ - In summary: (+5 → +4 → +5) <p>Step 3: Converting SO_3 to Concentrated H_2SO_4:</p> <p>The sulfur trioxide is absorbed in concentrated sulfuric acid (H_2SO_4) to form oleum ($\text{H}_2\text{S}_2\text{O}_7$), which is then diluted with water to produce concentrated sulfuric acid</p>

17.29	<p>understand how a catalytic converter decreases carbon monoxide and nitrogen monoxide emissions from internal combustion engines by:</p> <ul style="list-style-type: none"> i adsorption of CO and NO molecules onto the surface of the catalyst, resulting in the weakening of bonds and chemical reaction ii desorption of CO₂ and N₂ product molecules from the surface of the catalyst
	<p>Carbon monoxide, nitrogen dioxide and unburnt hydrocarbons are sources of pollution in car exhaust</p> <ul style="list-style-type: none"> - Carbon monoxide is toxic and interferes with oxygen transport in the body - Nitrogen monoxide is easily oxidised in the atmosphere to form nitrogen dioxide which is a respiratory irritant and contributes to the formation of acid rain
i and ii	<ol style="list-style-type: none"> 1. Molecules of carbon monoxide and nitrogen monoxide are adsorbed onto the surface 2. The bonds in both molecules are weakened causing them to react together to form carbon dioxide and nitrogen 3. The products are then desorbed from the surface of the catalyst <p>!Honeycomb-like structure of catalytic converter coated with a thin layer of catalyst metal (Platinum, Palladium, Rhodium) increases the surface area of catalyst</p>
17.30	<p>know that a homogeneous catalyst is in the same phase as the reactants and appreciate that the catalysed reaction will proceed via an intermediate species</p>
	<p>A homogeneous catalyst is</p> <ul style="list-style-type: none"> - in the same phase (physical state) as the reactants - reaction will proceed via an intermediate species <p>Transition metals can act as homogeneous catalysts because they can form various oxidation states (They can donate & receive electrons and can oxidize and reduce) This is because the ions contain partially filled sub-shells of d electrons that can easily lose or gain electrons</p>
17.31	<p>understand the role of Fe²⁺ ions in catalysing the reaction between I⁻ and S₂O₈²⁻ ions</p> <p>Fe²⁺ Ion Catalysts</p> <ul style="list-style-type: none"> - Transition metal ions can catalyse redox reactions, by acting as both oxidising agents and reducing agents due to their variable oxidation states - Example, Fe is often used as a catalyst due to its ability to form Fe(II) and Fe(III) ions, acting as a reducing agent and an oxidising agent <p>Iron(II) ions can catalyse reaction between I⁻ ions and peroxodisulfate ions, S₂O₈²⁻</p> <ul style="list-style-type: none"> - $S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{2-}$ - Originally, reaction is quite slow because the repulsion of two negative ions coming together hinders the reaction (high E_a) - When iron(II) ions are added to the reaction, the rate is much quicker - Starch is often added to this reaction, which will form a blue-black colour showing the formation of iodine - The addition of iron(II) ions reduces the peroxodisulfate to sulfate ions and produces iron(III) in the process - $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$ - The iron(III) ions will oxidise iodide ions to iodine and then are reduced once again to iron(II) - $2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+}$ <p>(+2 → +3 → +2)</p>

17.32	know the role of Mn ²⁺ ions in autocatalysing the reaction between MnO ₄ ⁻ and C ₂ O ₄ ²⁻ ions						
	<p>Mn²⁺ ions as an Autocatalyst</p> <ul style="list-style-type: none"> - Autocatalysis is the term used to describe a reaction which is speeded up by a product which acts as a catalyst for the reaction - Rate of reaction increases as reaction proceeds (unlike normal reactions where rate decreases as time goes on) due to production of an autocatalyst - However, rate eventually decreases as reaction proceeds as the reactants start to run out <p>Example: Reaction between manganate(VII) ions and oxalate (ethanedioate) ions</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="text-align: center; vertical-align: middle;">OX.</td> <td style="text-align: center; vertical-align: middle;">$C_2O_4^{2-}(aq) \longrightarrow 2CO_2(g) + 2e^-$</td> </tr> <tr> <td style="text-align: center; vertical-align: middle;">RED.</td> <td style="text-align: center; vertical-align: middle;">$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$</td> </tr> <tr> <td colspan="2" style="text-align: center; padding-top: 10px; border: 1px solid black; padding-bottom: 10px;"> $5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$ </td> </tr> </table> <p>Manganese(II) ions take part in a redox cycle between two different oxidation states (+2 → +3 → +2)</p> $4Mn^{2+} + MnO_4^- + 8H^+ \rightarrow 5Mn^{3+} + 4H_2O$ $2Mn^{3+} + C_2O_4^{2-} \rightarrow 2CO_2 + 2Mn^{2+}$ <p>This reaction is easily followed on a colorimeter as the rate at which the purple manganate(VII) ion is consumed accelerates with time</p>	OX.	$C_2O_4^{2-}(aq) \longrightarrow 2CO_2(g) + 2e^-$	RED.	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	$5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$	
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17.33	<p>CORE PRACTICAL 14</p> <p>The preparation of a transition metal complex.</p> <p>Further suggested practicals:</p> <ol style="list-style-type: none"> i prepare the different oxidation states of vanadium (17.18/19) ii investigate the equilibrium reaction in 17.21 iii carry out the reactions of transition metal ions with sodium hydroxide and ammonia solutions (17.22) iv carry out the ligand exchange reactions in 17.24 v investigate the kinetics of the reaction between MnO₄ and C₂O₄²⁻ in 17.32 						